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Preparation of polyamides

The present invention relates to a process for preparing a polyamide by reacting a mixture which comprises a monomer which has a nitrile group and has at least one other functional group capable of forming a carboxamide group, and comprises water, in the presence of titanium dioxide as catalyst, which comprises using titanium dioxide whose BET surface area, determined to the 10 German standard DIN 66 131 volumetrically by the multipoint method, is in the range from 5 to 35 m<sup>2</sup>/g.

Polyamides, in particular nylon-6 and nylon-6,6, are important industrial polymers.

15 WO 99/38906, WO 99/38908, and WO 01/09224 are examples of disclosures of preparation processes via reaction of a mixture which comprises a monomer which has a nitrile group and has at least one other functional group capable of forming a carboxamide 20 group, and comprises water, in the presence of titanium dioxide as catalyst.

It is pointed out here in WO 99/38906, WO 99/38908 and WO 01/09224 that the titanium dioxide is to have a BET surface 25 area of more than 40 m<sup>2</sup>/g, preferably more than 100 m<sup>2</sup>/g, since if the BET surface area selected is smaller the bed volume selected has to be higher to ensure sufficient catalyst activity. Examples of titanium dioxides mentioned in WO 99/38906, WO 99/38908, and WO 01/09224 therefore have BET surface areas of 46, 50, 73, and 30 116 m<sup>2</sup>/g.

Although the processes mentioned in WO 99/38906, WO 99/38908, and WO 01/09224 give polymer with properties which are good per se, it is desirable to reduce the titanium dioxide content of the 35 polymer which results when the catalyst becomes distributed in the material, even though this content is considerably lower than the level of contamination of the polymer when homogeneous catalysis is used. The higher the titanium dioxide content of the polymer, the higher the loss of catalyst per unit quantity of 40 polymer. Reduction of titanium dioxide content in the polymer is desirable in order to achieve longer catalyst operating time.

It is an object of the present invention to provide a process which permits the preparation of polyamides by reacting a mixture 45 which comprises a monomer which has a nitrile group and has at least one other functional group capable of forming a carboxamide group, and comprises water, in the presence of titanium dioxide

as catalyst in a manner which is technically simple and cost-effective, in particular without any reduction of catalyst activity when comparison is made with the known prior-art processes, eliminating the disadvantage mentioned.

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We have found that this object is achieved by the process defined at the outset.

Polyamides are homopolymers, copolymers, mixtures, and grafts derived from synthetic long-chain polyamides, and containing, in the main polymer chain, repeat carboxamide groups as a substantial constituent. Examples of these polyamides are nylon-6 (polycaprolactam), nylon-6,6 (polyhexamethyleneadipamide), nylon-4,6 (polytetramethyleneadipamide), nylon-6,10 15 (polyhexamethylenesebacamide), nylon-7 (polyenantholactam), nylon-11 (polyundecanolactam), nylon-12 (polydodecanolactam). These polyamides are known to have the generic name nylon. Polyamides also include what are known as aramids (aromatic polyamides), such as polymetaphenyleneisophthalamide (NOMEX<sup>®</sup>, 20 US-A-3,287,324) or polyparaphenyleneterephthalamide (KEVLAR<sup>®</sup>, US-A-3,671,542).

According to the invention, the polyamide is prepared using a mixture which comprises a monomer which has a nitrile group and 25 at least one, for example 1, 2, 3, 4, 5, preferably 1, 2, or 3, in particular 1, other functional group capable of forming a carboxamide group.

The functional group capable of forming a carboxamide group is 30 advantageously a carboxylic acid group or a functional group from which a carboxylic acid equivalent can be made available in the process of the invention for the purposes of forming a carboxamide group, examples being a nitrile group, a carboxylic ester group, a carboxamide group, or advantageously an amine 35 group, or a functional group from which an amine equivalent can be released in the process of the invention for the purposes of forming a carboxamide group. If the monomer has two or more of these functional groups capable of forming a carboxamide group, the groups in the monomer may be identical or different. It is 40 possible to use either one monomer or a mixture of two or more of these monomers, these being described in the same way as monomer for the purposes of the present invention.

In one preferred embodiment, use may be made of a monomer 45 selected from the group consisting of dinitrile, nitrilocarboxamide, nitrilocarboxylic acid, nitrilocarboxylic ester, aminonitrile, and mixtures of these. In one particularly

preferred embodiment, use is made of an aliphatic monomer. Monomers which have proved advantageous here are those in which the nitrile group and the other functional group capable of forming a carboxamide group are in alpha,omega positions, and in particular a monomer selected from the group consisting of alpha,omega-dinitrile, alpha,omega-nitrilocarboxamide, alpha,omega-nitrilocarboxylic acid, alpha,omega-nitrilocarboxylic ester, alpha,omega-aminonitrile, and mixtures of these.

- 10 Among the alpha,omega-aminonitriles, preference is given to those having from 4 to 12 carbon atoms, especially those having from 4 to 9 carbon atoms, in the alkylene radical, or an aminoalkylenearylenenitrile having from 8 to 13 carbon atoms, in particular those which, between the aromatic unit and the amino and nitrile group, have an alkylene group having at least one carbon atom. Among the aminoalkylenearylenenitriles, particular preference is given to those which have the amino and nitrile group in 1,4-positions in relation to the arylene system.
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- 20 The alpha,omega-aminonitriles used are more preferably linear alpha,omega-aminoalkylene nitriles, the alkylene radical  $(-\text{CH}_2-)_n$  preferably having from 4 to 12 carbon atoms, particularly preferably from 4 to 9 carbon atoms, examples being 5-amino-1-cyanopentane (6-aminocapronitrile),
- 25 6-amino-1-cyano hexane, 7-amino-1-cyano heptane, 8-amino-1-cyano octane, 9-amino-1-cyano nonane, particular preference being given to 6-aminocapronitrile.

- 30 6-Aminocapronitrile is usually obtained by using known processes to hydrogenate adiponitrile, for example those mentioned in WO 99/38906, WO 99/38908, and WO 01/09224.

Among the alpha,omega-dinitriles, preference is given to those having from 3 to 11 carbon atoms, especially those having from 3 to 8 carbon atoms, in the alkylene radical, or an alkylenearylenedinitrile having from 7 to 12 carbon atoms, in particular those which, between the aromatic unit and the two nitrile groups, have an alkylene group having at least one carbon atom. Among the alkylenearylenedinitriles, particular preference is given to those which have the two nitrile groups in 1,4-positions in relation to the arylene system.

The alpha,omega-dinitriles used are more preferably linear alpha,omega-alkylene nitriles, the alkylene radical  $(-\text{CH}_2-)_n$  preferably having from 3 to 11 carbon atoms, particularly preferably from 3 to 8 carbon atoms, examples being propane-1,3-dinitrile, butane-1,4-dinitrile (adiponitrile),

pentane-1,5-dinitrile, hexane-1,6-dinitrile,  
heptane-1,7-dinitrile, octane-1,8-dinitrile, particular  
preference being given to adiponitrile.

- 5 Among the alpha,omega-nitrilocarboxylic acids, preference is given to those having from 3 to 11 carbon atoms, especially those having from 3 to 8 carbon atoms, in the alkylene radical, or a nitriloalkylenearylene carboxylic acid having from 7 to 12 carbon atoms, in particular those which, between the aromatic unit and
- 10 the carboxylic acid group and nitrile group, have an alkylene group having at least one carbon atom. Among the nitriloalkylenearylene carboxylic acids, particular preference is given to those which have the carboxylic acid group and nitrile group in 1,4-positions in relation to the arylene system.
- 15 The alpha,omega-nitrilocarboxylic acids more preferably used are linear alpha,omega-nitriloalkylenecarboxylic acids, the alkylene radical  $(-\text{CH}_2-)_n$  preferably having from 3 to 11 carbon atoms, particularly preferably from 4 to 9 carbon atoms, examples being
- 20 5-nitrilo-1-pantanecarboxylic acid (5-cyanovaleric acid), 6-nitrilo-1-hexanecarboxylic acid, 7-nitrilo-1-heptanecarboxylic acid, 8-nitrilo-1-octanecarboxylic acid, 9-nitrilo-1-nonane-carboxylic acid, particularly preferably 5-cyanovaleric acid.
- 25 Among the alpha,omega-nitrilocarboxamides, preference is given to those having from 3 to 11 carbon atoms, especially those having from 3 to 8 carbon atoms, in the alkylene radical, or a nitriloalkylenearylene carboxamide having from 7 to 12 carbon atoms, in particular those which, between the aromatic unit and
- 30 the carboxamide group and nitrile group, have an alkylene group having at least one carbon atom. Among the nitriloalkylenearylene carboxamides, particular preference is given to those which have the carboxamide group and nitrile group in 1,4-positions in relation to the arylene system.
- 35 The alpha,omega-nitrilocarboxamides used are more preferably linear alpha,omega-nitriloalkylenecarboxamides, the alkylene radical  $(-\text{CH}_2-)_n$  preferably having from 3 to 11 carbon atoms, particularly preferably from 3 to 8 carbon atoms, examples being
- 40 5-nitrilo-1-pantanecarboxamide (5-cyanovaleramide), 6-nitrilo-1-hexanecarboxamide, 7-nitrilo-1-heptanecarboxamide, 8-nitrilo-1-octanecarboxamide, 9-nitrilo-1-nonane-carboxamide, particularly preferably 5-cyanovaleramide.
- 45 Among the alpha,omega-nitrilocarboxylic esters, preference is given to the abovementioned nitrilocarboxylic acids in the alpha,omega-nitrilocarboxylic acid component.

Preferred alcohol components of the ester are C1-C4-alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, or tert-butyl, in particular methyl.

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It is preferable to use 5-nitrilo-1-pantanecarboxylic esters (5-cyanovaleric esters), 6-nitrilo-1-hexanecarboxylic esters, 7-nitrilo-1-heptanecarboxylic esters, 8-nitrilo-1-octane-carboxylic esters, 9-nitrilo-1-nonanecarboxylic esters,

10 particularly preferably methyl 5-cyanovalerate.

Monomers which may be used with particular preference are those suitable for forming nylon-6, nylon-6,6, or copolymers of these, for example adiponitrile, 5-cyanovaleramide, 5-cyanovaleric acid,

15 C<sub>1</sub>-C<sub>4</sub>-alkyl cyanovalerates, 6-aminocapronitrile, or a mixture of these, in particular adiponitrile, 5-cyanovaleramide, 5-cyanovaleric acid, 6-aminocapronitrile, or mixtures of these, particularly preferably 6-aminocapronitrile, adiponitrile, or a mixture of these.

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If the monomer used comprises a compound in which the ratio between the molar total obtained from the nitrile group and the functional groups from which a carboxylic acid equivalent can be made available in the process of the invention for the purposes

25 of forming a carboxamide group, including the carboxylic acid groups themselves, and the molar total obtained from the amino groups and the functional groups from which an amino equivalent can be made available in the process of the invention for the purposes of forming a carboxamide group is outside the range of

30 from 0.9:1 to 1:0.9, for example as is the case with adiponitrile, 5-cyanovaleric acid, 5-cyanovaleramide, and alkyl 5-cyanovalerates, in which the ratio of the two molar totals to one another is 2:0, it is advantageous to use an addition of compounds suitable for forming polyamides so that the ratio of

35 the molar total obtained from the nitrile group and the functional groups from which a carboxylic acid equivalent can be made available in the process of the invention for the purposes of forming a carboxamide group, including the carboxylic acid groups themselves, and the molar total obtained from the amino

40 groups and the functional groups from which an amino equivalent can be made available in the process of the invention for the purposes of forming a carboxamide group is shifted into the range from 0.9:1 to 1:0.9.

45 In the case of a monomer selected from the group consisting of dinitrile, nitrilocarboxamide, nitrilocarboxylic acid, nitrilocarboxylic ester, and mixtures of these, it is

advantageous to use an addition of a polyfunctional, for example bi-, tri-, or tetrafunctional, in particular bifunctional, amine (i.e. a diamine), preferably in the case of a diamine so that the molar ratio between the monomer mentioned and the diamine is in 5 the range from 0.9:1 to 1:0.9, in particular from 0.95:1 to 1:0.95.

Diamines which may be used individually or in a mixture are in principle any diamines. Among these, preference is given to the 10 alpha,omega-diamines, preference among the latter being given to those having from 2 to 12 carbon atoms, especially those having from 2 to 10 carbon atoms, in the alkylene radical, or an alkylenearylenediamine having from 8 to 13 carbon atoms, in particular those which, between the aromatic unit and the two 15 amino groups, have an alkylene group having at least one carbon atom. Among the alkylenearylenediamines, particular preference is given to those which have the two amino groups in 1,4-positions in relation to the arylene system.

20 The alpha,omega-diamines used are more preferably linear alpha,omega-alkylenediamines, the alkylene radical (-CH<sub>2</sub>-)<sub>n</sub> preferably having from 2 to 12 carbon atoms, particularly preferably from 2 to 10 carbon atoms, examples being 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 25 1,5-diaminopentane, 1,6-diaminohexane (hexamethylenediamine), 1,7-diaminoheptane, 1,8-diaminoctane, 1,9-diaminononane, 1,10-diaminodecane, particularly preferably hexamethylenediamine.

More preferred alpha,omega-diamines are alpha,omega-alkylene-30 diamines, the alkylene radical preferably having from 2 to 12 carbon atoms, particularly preferably from 2 to 10 carbon atoms, and at least one carbon atom of the alkylene chain having substitution, preferably by a C<sub>1</sub>-C<sub>4</sub>-alkyl radical, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, or 35 tert-butyl, in particular methyl, an example being 2-methyl-1,5-diaminopentane. An example of a method of obtaining 2-methyl-1,5-diaminopentane is hydrogenation of the by-product 2-methylglutaronitrile arising during the preparation of adiponitrile by double hydrocyanation of butadiene.

40 In addition to the monomer which has a nitrile group and has at least one other functional group capable of forming a carboxamide group, use may be made of other compounds known to be used as a monomer for preparing polyamides, preferably those selected from 45 the group consisting of lactams, omega-aminocarboxylic acids, omega-aminocarboxamides, omega-aminocarboxylic salts, omega-aminocarboxylic esters, equimolar mixtures of diamines and

dicarboxylic acids, dicarboxylic acid/diamine salts, and mixtures of these monomers.

Additional compounds of this type which may be used are

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a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>18</sub>, arylaliphatic or preferably aliphatic lactam, in monomeric or oligomeric form, for example enantholactam, undecanolactam, dodecanolactam, or caprolactam, in particular caprolactam,

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a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>3</sub>-C<sub>18</sub>, aminocarboxylic acid, in monomeric or oligomeric form, for example 6-aminocaproic acid, 11-aminoundecanoic acid, or else salts of these, such as alkali metal salts, e.g. lithium salts, sodium salts, potassium salts,

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a C<sub>2</sub>-C<sub>20</sub> amino amide, in monomeric or oligomeric form, such as 6-aminocaproamide, 11-aminoundecanamide,

esters, in monomeric or oligomeric form, preferably C<sub>1</sub>-C<sub>4</sub>-alkyl

20 esters, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl esters, of C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>3</sub>-C<sub>18</sub>, aminocarboxylic acids, for example 6-aminocaproic esters, such as methyl 6-aminocaproate, 11-aminoundecanoic esters, such as methyl 11-aminoundecanoate,

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a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>12</sub>, alkyldiamine, in monomeric or oligomeric form, for example tetramethylenediamine or preferably hexamethylenediamine,

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with a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>14</sub>, aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid, or adipic acid,

a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>12</sub>, alkyldiamine, in monomeric or

oligomeric form, for example tetramethylenediamine or preferably

35 hexamethylenediamine,

with a C<sub>8</sub>-C<sub>20</sub>, preferably C<sub>8</sub>-C<sub>12</sub>, aromatic dicarboxylic acid or derivatives thereof, such as chlorides, for example

2,6-naphthalenedicarboxylic acid, preferably isophthalic acid, or

40 terephthalic acid,

a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>12</sub>, alkyldiamine, in monomeric or oligomeric form, for example tetramethylenediamine or preferably hexamethylenediamine,

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with a C<sub>9</sub>-C<sub>20</sub>, preferably C<sub>9</sub>-C<sub>18</sub>, arylaliphatic dicarboxylic acid or derivatives thereof, such as chlorides, for example o-, m-, or p-phenylenediacetic acid,

5 a C<sub>6</sub>-C<sub>20</sub>, preferably C<sub>6</sub>-C<sub>10</sub>, aromatic diamine, in monomeric or oligomeric form, for example m- or p-phenylenediamine,

with a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>14</sub>, aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid, or adipic acid,

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a C<sub>6</sub>-C<sub>20</sub>, preferably C<sub>6</sub>-C<sub>10</sub>, aromatic diamine, in monomeric or oligomeric form, for example m- or p-phenylenediamine,

with a C<sub>8</sub>-C<sub>20</sub>, preferably C<sub>8</sub>-C<sub>12</sub>, aromatic dicarboxylic acid or

15 derivatives thereof, such as chlorides, for example

2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or terephthalic acid,

20 a C<sub>6</sub>-C<sub>20</sub>, preferably C<sub>6</sub>-C<sub>10</sub>, aromatic diamine, in monomeric or oligomeric form, for example m- or p-phenylenediamine,

with a C<sub>9</sub>-C<sub>20</sub>, preferably C<sub>9</sub>-C<sub>18</sub>, arylaliphatic dicarboxylic acid or derivatives thereof, such as chlorides, for example o-, m- or p-phenylenediacetic acid,

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a C<sub>7</sub>-C<sub>20</sub>, preferably C<sub>8</sub>-C<sub>18</sub>, arylaliphatic diamine, in monomeric or oligomeric form, for example m- or p-xylylenediamine,

30 with a C<sub>2</sub>-C<sub>20</sub>, preferably C<sub>2</sub>-C<sub>14</sub>, aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid, or adipic acid,

a C<sub>7</sub>-C<sub>20</sub>, preferably C<sub>8</sub>-C<sub>18</sub>, arylaliphatic diamine, in monomeric or oligomeric form, for example m- or p-xylylenediamine,

35 with a C<sub>6</sub>-C<sub>20</sub>, preferably C<sub>6</sub>-C<sub>10</sub>, aromatic dicarboxylic acid or derivatives thereof, such as chlorides, for example  
2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or terephthalic acid,

40 a C<sub>7</sub>-C<sub>20</sub>, preferably C<sub>8</sub>-C<sub>18</sub>, arylaliphatic diamine, in monomeric or oligomeric form, for example m- or p-xylylenediamine,

with a C<sub>9</sub>-C<sub>20</sub>, preferably C<sub>9</sub>-C<sub>18</sub>, arylaliphatic dicarboxylic acid or derivatives thereof, such as chlorides, for example o-, m- or

45 p-phenylenediacetic acid,

or else homopolymers, copolymers, mixtures, and grafts of these monomers or oligomers.

Oligomers which may be used with advantage are dimers, trimers, 5 tetramers, pentamers, or hexamers of these monomers, or of mixtures of these monomers.

Preference is given here to those additional compounds which during the polymerization give the polyamides nylon-6, nylon-6,6, 10 nylon-4,6, nylon-6,10, nylon-7, nylon-11, nylon-12, or the aramids polymetaphenyleneisophthalamide or polyparaphenylene-terephthalamide, in particular nylon-6 or nylon-6,6, examples being caprolactam, adipic acid, and hexamethylenediamine.

15 Lactams can be obtained by reacting a cyclic ketone with hydroxylamine to give the corresponding oxime and then using Beckmann rearrangement, or from the corresponding amino nitriles via hydrolytic cyclization prior to or during the polymerization, in particular in the presence of catalysts, such as titanium 20 dioxide, in a manner known per se.  
The preparation of omega-aminocarboxylic acids, omega-amino-carboxamides, omega-aminocarboxylic salts, and omega-aminocarboxylic esters is known per se. They may be prepared from the corresponding amino nitriles prior to or during 25 the polymerization, for example.

The preparation of dicarboxylic acids is known per se. For example, they may be obtained from the corresponding dinitriles prior to or during the polymerization.  
30 Diamines may be prepared in a manner known per se, for example by hydrogenating the corresponding dinitriles.

The reaction may also advantageously take place with addition of 35 chain regulators known per se, such as monocarboxylic acids, preferably C<sub>1</sub>-C<sub>10</sub> alkanemonocarboxylic acids, e.g. acetic acid or propionic acid, preferably C<sub>5</sub>-C<sub>8</sub> cycloalkanemonocarboxylic acids, such as cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, or preferably benzene- or naphthalenemonocarboxylic acids, such 40 as benzoic acid, naphthalenecarboxylic acid, or such as dicarboxylic acids, preferably C<sub>2</sub>-C<sub>10</sub> alkanedicarboxylic acids, e.g. adipic acid, azelaic acid, sebacic acid, or decane-dicarboxylic acid, preferably C<sub>5</sub>-C<sub>8</sub> cycloalkanedicarboxylic acids, e.g. 1,4-cyclohexanecarboxylic acid, preferably benzene- or 45 naphthalenecarboxylic acids, e.g. isophthalic acid, terephthalic acid, 2,6-naphthalenedicarboxylic acid, or monoamines, preferably C<sub>1</sub>-C<sub>10</sub> alkane monoamines, preferably C<sub>5</sub>-C<sub>8</sub> cycloalkane monoamines,

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e.g. cyclopentylamine, cyclohexylamine,  
4-amino-2,2,6,6-tetramethylpiperidine, or a benzene or  
naphthalene monoamine, e.g. aniline, naphthylamine, or diamines,  
preferably C<sub>2</sub>-C<sub>10</sub> alkanediamines, e.g. hexamethylenediamine,  
5 preferably C<sub>5</sub>-C<sub>8</sub> cycloalkanediarnines, e.g. 1,4-cyclohexanediamine,  
preferably benzene-, naphthalene-, or xylylidenediamines, e.g.  
o-xylylidenediamine, m-xylylidenediamine, p-xylylidenediamine, or  
a mixture of these known chain regulators. These chain regulators  
may be used in a manner known per se, preferably in amounts in  
10 the range of from 1 to 55 µg/g of polyamide, particularly  
preferably from 1 to 30 µg/g of polyamide, in particular from 1  
to 15 µg/g of polyamide.

According to the invention, use is made of a mixture which  
15 comprises a monomer which has a nitrile group and has at least  
one other functional group capable of forming a carboxamide  
group, and comprises water.

The molar ratio between monomer, including any added additional  
20 compounds capable of polyamide formation, and water should  
advantageously be in the range from 1:1 to 1:20, preferably from  
1:2 to 1:15, in particular from 1:2 to 1:10.

In one preferred embodiment, the mixture should comprise only  
25 6-aminocapronitrile as monomer, and the molar ratio between  
6-aminocapronitrile and water should advantageously be in the  
range from 1:1 to 1:20, preferably from 1:2 to 1:15, in  
particular from 1:2 to 1:10.

30 In another preferred embodiment, the mixture should comprise only  
adiponitrile and hexamethylenediamine as monomer, and the molar  
ratio of the molar total obtained from adiponitrile and  
hexamethylenediamine to water should advantageously be in the  
range from 1:1 to 1:20, preferably from 1:2 to 1:15, in  
35 particular from 1:2 to 1:10.

In another preferred embodiment, the mixture should comprise only  
6-aminocapronitrile, adiponitrile, and hexamethylenediamine as  
monomer, and the molar ratio of the total obtained from  
40 6-aminocapronitrile, adiponitrile, and hexamethylenediamine to  
water should advantageously be in the range from 1:1 to 1:20,  
preferably from 1:2 to 1:15, in particular from 1:2 to 1:10.

For the inventive reaction of the mixture to give a polyamide,  
45 the monomer here and the water may be introduced to the reaction  
apparatus together or separately.

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According to the invention, the polyamide is prepared in the presence of titanium dioxide as catalyst, the BET surface area of the titanium dioxide, determined volumetrically to the German standard DIN 66 131 by the multipoint method, being in the range 5 from 5 to 35 m<sup>2</sup>/g, preferably in the range from 15 to 35 m<sup>2</sup>/g.

The titanium dioxide should advantageously be entirely in the anatase form, although it has hitherto also been found possible for from 0 to 30% by weight, advantageously from 20-30% by 10 weight, of the titanium dioxide used, based on the total titanium dioxide used, to be composed of rutile (the remainder being anatase).

The titanium dioxide may advantageously be used in the form of 15 moldings, such as extrudates or pellets. Particular preference is given to pellets of average length from 5 to 20 mm, in particular about 10 mm, and of average diameter from 1 to 6 mm, in particular about 4 mm.

20 The cutting hardness is not critical per se and may be in the range of small values, such as from 2 N to 10 N, of moderate values, such as from above 10 N to 20 N, or else of higher values, such as above 20 N or above 25 N.

25 The catalysts may be prepared from commercially available titanium dioxide powders. A portion of the titanium dioxide may be replaced here by other oxides, such as tungsten oxide. In the case of tungsten oxide use may advantageously be made of amounts of up to 40% by weight, preferably up to 30% by weight, in 30 particular from 15 to 25% by weight, based in each case on the entirety of titanium dioxide and tungsten oxide.

The process of conversion to give catalysts may take place by methods known per se, for example those described in Ertl, 35 Knözinger, Weitkamp: "Handbook of heterogeneous catalysis", VCH Weinheim, 1997, pp. 98 et seq.

The reaction of the process of the invention may be carried out batchwise, or preferably continuously.

40 In the case of continuous operation, the reaction may be carried out in the reactors known per se for preparing polyamides, for example in one or more flow tubes, in one or more stirred tanks, or in combinations of apparatus of this type.

In one preferred embodiment, the reaction of the process of the invention may be carried out in at least one flow tube, and the titanium dioxide used as catalyst may be used in the form of moldings in combination with metallic packings.

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The metallic packings preferably have a structure of corrosion-resistant metals, in particular corrosion-resistant steel. These packings may have any suitable shape. They are particularly preferably Raschig rings. These Raschig rings

10 preferably have an average diameter in the range from 2 to 6 mm, preferably about 3 mm.

The size of the titanium dioxide moldings, preferably the titanium dioxide pellets, should advantageously be selected so  
15 that firstly it is possible to remove the moldings mechanically without difficulty via filter and screen, and secondly the pressure increase brought about by the flow resistance due to the increased density of solids in the reactor is within industrially controllable limits. The average bulk density in the flow tube  
20 reactor may be adjusted via a suitable ratio of titanium dioxide molding to metallic packing. Mixtures of titanium dioxide moldings and metallic packings may also be present here in the flow tube. It is preferable for there to be layering of the titanium dioxide moldings and the metallic packings in the flow  
25 tube. It is then advantageously possible for a layer of titanium dioxide moldings to be followed by a layer of metallic packings in the direction of flow. There may also be an alternating layer sequence of the two moldings with from 2 to 20, preferably from 3 to 15, layers.

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In another particularly preferred embodiment, the reaction of the process of the invention may be carried out in at least one flow tube, and the titanium dioxide used as catalyst may be in the form of moldings in combination with internals bearing the  
35 catalyst and secured to the flow tube. These catalyst-bearing internals may extend over the entire cross section of the tube, or only over portions of the cross section of the tube, for example a segment or an annulus. These internals may have any desired shape. Examples of those used advantageously are nets,  
40 perforated plates, and perforated sheets, such as films or metal panels.

The internals preferably have a structure of corrosion-resistant metals, in particular corrosion-resistant steel.

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The size of the titanium dioxide moldings, preferably of the titanium dioxide pellets, should advantageously be selected so that firstly it is possible to remove the moldings mechanically without difficulty via filter and screen, and secondly the 5 pressure increase brought about by the flow resistance due to the increased density of solids in the reactor is within industrially controllable limits. The average bulk density in the flow tube reactor may be adjusted via a suitable ratio of titanium dioxide molding to catalyst-bearing internals.

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The process of the invention for preparing a polyamide by reacting a mixture which comprises a monomer which has a nitrile group and has at least one other functional group capable of forming a carboxamide group, and comprises water, may take place 15 in one or more, for example two, three, or four, stages, the process parameters for which, such as pressure and temperature, may differ. The ammonia arising during the reaction may advantageously be removed between each of the stages.

20 Processes for preparing a polyamide by reacting a mixture which comprises a monomer which has a nitrile group and has at least one other functional group capable of forming a carboxamide group, and comprises water, in the presence of titanium dioxide as catalyst are known per se, for example from WO 99/38906, 25 WO 99/38908, and WO 01/09224, the content of which is hereby incorporated into the present description by way of reference. The advantage of the process of the invention over the processes described in WO 99/38906, WO 99/38908, and WO 01/09224 is achievable simply by replacing the titanium dioxide used in one 30 stage of the stages described in WO 99/38906, WO 99/38908, and WO 01/09224 with a titanium dioxide of the present invention. In one particularly advantageous embodiment, all of the titanium dioxide used as catalyst in the processes of WO 99/38906, WO 99/38908, and WO 01/09224 should be replaced by a titanium dioxide of the 35 present invention.

Compared with the processes of WO 99/38906, WO 99/38908, and WO 01/09224, the process of the invention gives a polyamide with reduced titanium dioxide content while other process parameters, 40 such as pressure, temperature, material flow rates, concentrations, and starting materials remain the same.

Surprisingly, it has been found here that the reduction in catalyst activity claimed in the prior art for the BET surface 45 area of the catalyst of the present invention does not occur, the catalyst activity in the process of the invention in fact being

just as high as in the processes described in WO 99/38906, WO 99/38908, and WO 01/09224.

#### Examples

5

All examples and comparative examples were carried out in a multistage system as shown diagrammatically in WO 99/38908, Fig. 1.

10 The reactor (1) used was a tube with void volume 60 liters and internal length 5 m.

The stage (2) used was a 100 l centrifugal separator.

15 The stage (3) used was a tube packed with Raschig rings (diameter 6 mm, length 6 mm) and having void volume of 30 liters and internal length 2.5 m.

The stage (4) used was a centrifugal separator with volume 20 264 liters, from which the polymer melt was discharged as an extrudate (A) with the aid of a gear pump.

The process parameters set were the following:

25 Stage (1):

Mass flow rate:	20 kg/h
6-Aminocapronitrile/water:	1:6 mol/mol
Pressure:	80 bar
Temperature:	240°C

30

Stage (2):

Level:	15%
Pressure:	30 bar
Temperature:	250°C

35

Stage (3)

Water addition:	10% by weight, based on material flow rate in stage (1)
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Pressure: 45 bar

40 Temperature:

250°C

Stage 4

Level:	25%
Pressure:	1 bar
45 Temperature:	260°C

## 15

The following catalysts were used in stage (1):

Comparative example 1

5 Stage (1) was packed entirely with a titanium dioxide whose BET surface area was 50 m<sup>2</sup>/g, and whose extrudate length was in the range from 2 to 14 mm, and whose extrudate thickness was 4 mm, as in WO 99/38908, p. 29, lines 28-31.

10 Example 1

The titanium dioxide pellets used in comparative example 1 were heat-conditioned at 500°C for 20 hours prior to installation and had a BET surface area of 30 m<sup>2</sup>/g.

15

Example 2

Stage (1) was subdivided into five equal-length segments each of length 1 m, at the inlet to each of which there was a screen made 20 from stainless steel (1.4571), (mesh width 2 mm). Each segment was filled with the catalyst of example 1, and the segments were placed together so that stage (1) of example 2 had the same shape as stage (1) of example 1 and comparative example 1.

25 The results obtained were as follows:

		Titanium dioxide content of polymer [ppm by weight; determined as titanium]				
		After 24 h	After 48 h	After 96 h	After 144 h	After 240 h
30	Example 1	3	2	2	1	1
	Example 2	2	1	--	--	--
	Comp.ex.1	7	6	5	4	4

35 Table 1

--: below the 1 ppm detection limit

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